# **Experimental Plan for DPC/Overpack Performance in a Repository**

**Fuel Cycle Research & Development** 

Prepared for
U.S. Department of Energy
Office of Used Nuclear Fuel Disposition
A. Ilgen, D. Enos, C. Bryan,
R. Rechard, and E. Hardin
Sandia National Laboratories
September 29, 2014

FCRD-UFD-2014-000596



#### DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.





#### **SUMMARY**

This report outlines the laboratory corrosion tests for the materials used in the dual purpose canisters (DPC). The proposed testing program is designed to assess whether structural integrity of a stainless steel basked will be preserved in case of an early breach (flooding with groundwater) during direct disposal of a DPC. Additionally, we are addressing several of the most uncertain areas concerning material behavior in a repository, particularly corrosion rates of the corrosion-resistant materials under anoxic conditions, potential for the localized corrosion and its feedback to the mechanical strength of the waste package components. The materials proposed for testing are stainless steels 304/304L and 316/316L – widely used in the existing DPCs, and prospective overpack materials Hastelloys C-4 and C-22. These results will contribute to the overall evaluations on the feasibility of the direct disposal of DPCs.

# **CONTENTS**

SUN	MMAF	RY	iii
AC	RONY	MS	vii
1.	Mot	ivation for the experimental testing	1
2.	Geo	chemical systems selected for testing	2
3.	Mat	erials	4
	3.1	Metals	4
	3.2	Groundwater composition	5
	3.3	Bentonite buffer	6
4.	Phys	sico-chemical variables	7
5.	Test	ing protocols and analytical methods	7
	5.1	Measurements of the general corrosion rates	7
	5.2	Localized corrosion tests	9
	5.3	Tests for the environmentally assisted cracking	10
6.	Sum	mary and expected outcomes of the laboratory testing program	12
7.	Refe	erences	13

## **FIGURES**

Figure 1. Corrosion interfaces in a waste package	3
Figure 2. Corrosion beneath a crack or a pin-hole in the overpack.	4
Figure 3. Degradation sequence of internal basket structure and commercial spent nuclear fuel after waste package breach	5
Figure 4. Schematic representation of an anodic polarization curve for a passive metal susceptible to localized corrosion. Indicated on the figure are the open circuit potential (i.e., the rest potential), the pitting potential, the repassivation potential, and the passive current density	10
TABLES	
Table 1. Proposed representative chemical compositions of the groundwater (shale data is from Blondes et al., 2014, and granite data - from Frape et al., 2003)	6
Table 2. Mass fraction (%) of minerals for FEBEX, MX-80 bentonite, and Wyoming bentonite (From Jové Colón et al., 2014, and references therein)	6

# **ACRONYMS**

ASTM American Society for Testing and Materials

DPC Dual Purpose Canister

DCPD Direct Current Potential Drop

EPRI Electric Power Research Institute

FEBEX Full-scale Engineered Barriers Experiment

ICP-MS Inductively Coupled Plasma Mass Spectrometry

NACE National Association of Corrosion Engineers

NRC Nuclear Regulatory Commission

NIST National Institute of Standard and Technology

SCC Stress Corrosion Cracking

SOP Standard Operating Procedure

TDS Total Dissolved Solids

UNF Used Nuclear Fuel

UFD Used Fuel Disposition

# EXPERIMENTAL PLAN FOR DPC/OVERPACK PERFORMANCE IN A REPOSITORY

## 1. Motivation for the experimental testing

Predicting structural integrity of the stainless steel basket within a dual purpose canister (DPC) is a critical step in determining potential disposability of a waste package. The function of the basket is to maintain spent nuclear fuel configuration to prevent criticality during the required repository performance period of up to 10,000 years. The DPC body is usually constructed from the 1.27 to 1.59 cm (1/2 to 5/8 inch) thick stainless steel, and is not expected to provide structural strength for handling and emplacement, and, likely, corrosion resistance to isolate the waste for the required repository performance period. Therefore, an overpack would be required to resist damage during handling, emplacement, and long term isolation of used nuclear fuel (UNF). The main goal of the proposed testing is to predict realistic degradation rates of the stainless steel basket in case of an early breach (penetration and flooding with groundwater) of both the overpack, and the stainless steel canister. A few additional screening experiments are proposed to address corrosion of the potential overpack materials.

Preliminary screening of the existing DPC designs indicates that a significant number of them use stainless steel materials for the basket components. Under favorable physico-chemical conditions, they may potentially last for the required performance period of 10,000 years. A rough estimate of the expected loss of thickness of a stainless steel plate or sheet, after 10,000 years of exposure to ground water, is 0.01 to 1 mm (1-sided surface retreat). This estimate is based on the following assumptions:

- Anoxic conditions, non-corrosive water composition, and pH >4
- Estimated stainless steel corrosion rates for anoxic conditions are 0.001 to 0.1  $\mu$ m yr<sup>-1</sup> over the temperature range 30 to 80°C (Kursten et al. 2004)
- Localized corrosion (e.g., pitting) may occur but does not cause loss of structural integrity
- Crevice corrosion and stress corrosion cracking do not occur, or if they do occur damage to the basket does not impact structural integrity
  - · Microbially influenced corrosion does not occur
- Hydrogen that evolves at corroding surfaces diffuses away and does not accumulate in the uncorroded steel, so the extent of any hydrogen-embrittlement or hydrogen-induced cracking is not significant
- Radiolysis products (e.g., hydrogen peroxide  $H_2O_2$ ) predominantly react with uranium (IV) oxide  $UO_2$  in the spent nuclear fuel, or recombine, and do not react with basket materials to any significant extent because the cladding is mostly intact

The goal of the proposed experimental testing is to evaluate the validity of some of the assumptions listed above. Additionally we address some of the key areas of uncertainty associated with predicting the evolution of the physico-chemical conditions in a repository. These uncertain areas are:

Title Date

- Changes in redox conditions, temperature, hydrogen buildup/diffusion, interactions between products of corrosion (e.g., ferrous iron) and the clay buffer
- Diffusion of corrosion-active species (e.g., chloride or sulfide) through buffer material, and potential effects on long-term corrosion rate
  - Feedbacks between hydrogen production and transport
- Radiation effects on the corrosion environment, particularly in anoxic repository settings, from radicals produced by radiolysis (e.g., hydrogen peroxide)
- Competition for oxidizing radicals between the UNF and container materials and aspects of container design and fabrication that can affect corrosion:
  - o Effects of thermal treatments and welding of the basket
  - o Metallurgical modifications due to long-term radiation flux or thermal aging

The main goal of the proposed testing is to provide additional evidence for (non)feasibility of the direct disposal of DPCs. If the results of these experiments indicate overall corrosion rates of the DPC (particularly, basket) materials are sufficiently low to last up to 10,000 years, more detailed testing would have to be done taking into account the exact disposal system designs, and the coupled mechanical (stress) and chemical effects under the exact geochemical conditions of a proposed disposal site. These future investigations should therefore focus on the container-specific corrosion rates. Corrosion processes are complex, and there are no existing mechanistic process models that could more reliably predict corrosion rates.

# 2. Geochemical systems selected for testing

The tests are designed to evaluate corrosion behavior for the container materials during the postclosure period. Following closure and backfill, the conditions are expected to be oxic for a short (several years) period of time. Once all residual oxygen is consumed, the conditions will be anoxic in a low-permeability host media with backfill/buffer materials for the remainder of the repository performance period. Therefore, understanding the anaerobic corrosion rates and mechanisms of the materials of interest is critical.

Conceptually, processes at several geochemical interfaces control the corrosion rates and, therefore, expected performance of the package. The conceptual view of these interfaces is given in Figure 1. The exact local geochemical conditions will differ, and depend on the considered failure/performance scenario. For example, chemical composition of the groundwater flooding the package would differ depending on whether or not the bentonite buffer is breached. Below we identify several failure/performance scenarios, which we consider in our proposed corrosion testing.

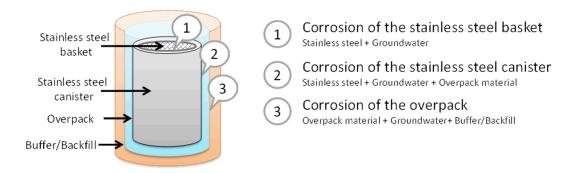


Figure 1. Corrosion interfaces in a waste package

Scenario 1 (basket performance evaluation): Buffer, overpack, and canister are breached – the groundwater from the geologic formation floods the canister. The composition of the groundwater is not affected by the bentonite buffer.

Scenario 2 (basket performance evaluation): Buffer is intact, overpack and canister are cracked, and the composition of the groundwater diffusing through the buffer is in chemical equilibrium with the mineralogical assemblage of the bentonite buffer material.

Scenario 3 (canister performance evaluation): Overpack and bentonite buffer are breached. A pin-hole or a thin crack in the overpack has formed, and the stainless steel canister is corroding in the anaerobic conditions in contact with the formation water. In this case the diffusion of the corrosion product - hydrogen gas - is limited by the immediate proximity of the intact metallic overpack (Figure 2.), and therefore hydrogen-embrittlement may become important. The composition of the groundwater is unaffected by the interaction with the bentonite buffer material.

Scenario 4 (canister performance evaluation): Same as Scenario 3, except the bentonite buffer is intact, so the composition of the groundwater is in chemical equilibrium with the bentonite buffer.

Scenario 5 (overpack performance evaluation): Bentonite buffer has failed, the overpack material is undergoing anaerobic corrosion in contact with groundwater, the composition of the groundwater is unaffected by the interaction with the bentonite buffer material.

Scenario 6 (overpack performance evaluation): Nothing is breached. The overpack material is undergoing anaerobic corrosion in contact with groundwater and compact bentonite buffer. For all outlined scenarios we propose to measure general and localized corrosion rates under the relevant conditions.

Title
4 Date

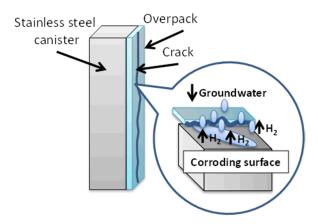


Figure 2. Corrosion beneath a crack or a pin-hole in the overpack

#### 3. Materials

#### 3.1 Metals

This test plan focuses on the stainless steels 304/304L and 316/316L. The exact samples (e.g. thicknesses, presence of welds and mechanically stressed zones) are selected to represent various components of the DPC baskets and outer shell. We consider a basket constructed from 5/16" (7.94 mm) think stainless steel sheets by welding a series of perpendicular and parallel plates to form an array of storage cells (NRC, 2014). One of the basket degradation scenarios is illustrated in Figure 3 (original source – Disposal criticality analysis methodology topical report, 1998). The basket failure is initiated at the locations of mechanical stresses and welds.

The prospective overpack materials, included in this round of testing, are corrosion resistant nickel alloys (Hastelloys C-4 and C-22) – we particularly focus on evaluating chemical behavior of the passive films, and the localized corrosion behavior of these materials under anoxic conditions. The Hastelloys are considered for the experimental testing within the failure/performance scenarios 3, 4, 5, and 6 outlined above. In addition to Hastelloys, we also consider copper and carbon steel for the scenarios 3, and 4.

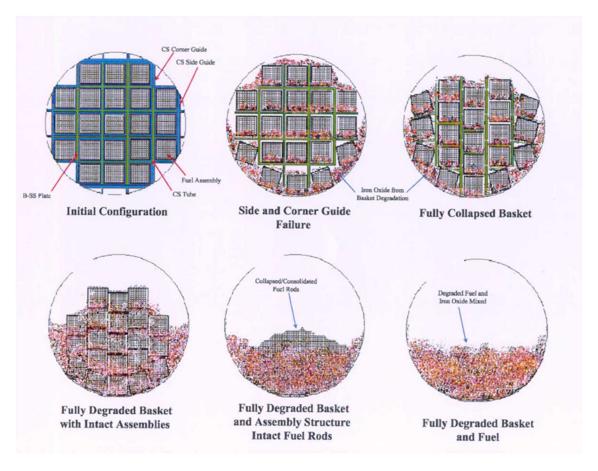


Figure 3. Degradation sequence of internal basket structure and commercial spent nuclear fuel after waste package breach

# 3.2 Groundwater composition

For the proposed tests and all outlined failure scenarios, we will use synthetic groundwater. The chemical composition of the synthetic groundwater is representative of the known sedimentary (shale) and crystalline (granite) geological formations (Blondes et al., 2014, Frape et al., 2003). When the failure scenario considers that the bentonite buffer is intact (scenarios 2, 4 and 6), the composition of the synthetic groundwater will be adjusted to reflect thermodynamic equilibrium concentrations after groundwater has passed through the bentonite buffer. Due to the large variability in the total dissolved solids (TDS) reported for the natural groundwater, and taking into account that corrosion rates are generally enhanced as the salt content is increased, we selected two representative compositions for two general repository types (shale and granite). One proposed water composition reflects the mid-range with regards to TDS, while another water type represents the high-TDS member. The four proposed water compositions are shown in Table 1. To reflect the geochemical conditions when the bentonite buffer is performing (e.g. failure/performance scenarios 2, 4, and 6), the water samples will be either equilibrated with the bentonite material prior to the corrosion tests or the tests will be done in the bentonite slurry. Given the complexity, and the site-specificity of the natural organic matter (potentially,

important for corrosion in a shale repository), we do not include any organic ligands in the proposed groundwater compositions.

Table 1. Proposed representative chemical compositions of the groundwater (shale data is from Blondes et al., 2014, and granite data - from Frape et al., 2003)

Constituent		Sha	ale	Gra	anite
		Shale-1	Shale-2	Granite-1	Granite-2
	TDS	50,990	249,150	53,480	250,360
	$Ca^{2+}$	2,044	12,983	5,450	63,800
	Na <sup>+</sup>	16,635	80,430	10,100	18,500
-1	$\mathrm{Mg}^{2+}$	624.66	2,689	5,260	24
$({\rm mg}\ L^{\text{-}1})$	$K^{+}$	215.11		57.6	371
(m	Cl <sup>-</sup>	30,349	152,817	32,143	166,200
	Br <sup>-</sup>			244	1,200
	$SO_4^{2-}$	996.97	207.97	<1	265
	HCO <sub>3</sub> -	340.25	24.13	54	0

### 3.3 Bentonite buffer

The clay buffer material proposed for our testing is bentonite clay, as it is a conventional buffer material choice for both shale and some granite repositories. The typical composition of the bentonite buffer material is shown in Table 2.

Table 2. Mass fraction (%) of minerals for FEBEX, MX-80 bentonite, and Wyoming bentonite (From Jové Colón et al., 2014, and references therein)

Mineral	FEBEX bentonite	MX-80 bentonite	Wyoming bentonite
Calcite	trace	0	
Illite	0.0	1	
Smectite	$92 \pm 3$	87	72
Chlorite	0.8	0	
Quartz	2 ± 1	3	1
K-Feldspar	trace	3	
Cristobalite	2 ± 1	0	2
Plagioclase	2 ± 1	0	9
Pyrite	0.02	0.25	0.4
Mica		4	
Gypsum	0.14	0.7	
Clinoptilolite			13
Biotite			3

# 4. Physico-chemical variables

The known physico-chemical corrosion drivers are moisture, pH, temperature, presence of oxidizing species, and the concentrations of chloride and sulfide ions. In the proposed testing program we assume saturated conditions (activity of water ~1), pH is nearly constant, and its value is selected based on the chemical equilibrium between the groundwater and either shale or granite mineral assemblages, or the bentonite buffer material. We assume that temperature of the package will evolve with time; however the proposed experimental work will be done at a constant temperature to measure anaerobic corrosion rates as they reach the steady state. Therefore, we propose to evaluate anoxic corrosion rates at constant temperature and pH values. while varying chloride concentrations, sulfide concentrations, and also testing how the presence of water-saturated bentonite buffer affects the corrosion rates and corrosion products. To determine the effects of the physical and thermal stress on the modes and rates of corrosion, we will include welded and U-bent samples, along with fresh and passivated metal coupons of stainless steels 304/304L and 316/316L, and Hastelloys C-4 and C-22. We will also assess whether limited diffusion (failure/performance scenarios 3 and 4) will create conditions favorable for the hydrogen embrittlement of the stainless steel canister. The concentrations of chloride will be varied from 100 to 100,000 mg L<sup>-1</sup> which covers the likely ranges in both granite and shale repository types (Hardin et al., 2014). The maximum concentration of dissolved (bi)sulfide ion will be fixed by the presence of pyrite mineral in the relevant experimental systems.

# 5. Testing protocols and analytical methods

The following section provides an overview of the proposed tests and analytical methods for determining the general and localized corrosion rates. In addition to the standard corrosion tests detailed below, we propose to measure aqueous concentrations of the dissolved iron, nickel, and chromium, and perform detailed chemical and mineralogical characterization of the corrosion products. The aqueous analysis (down to sub-ppb level) will be done using inductively coupled plasma mass spectrometry (ICP-MS). For the corrosion product characterization we propose using micro- and grazing incidence X-ray fluorescence and diffraction. The results of these analyses will be used to constrain the exact oxidation-precipitation-dissolution reactions to guide the interpretation of the electrochemical data. The corrosion batch tests will be performed using Parr reactors, aged at a constant temperature. To limit the access of atmospheric oxygen, the reactors will be loaded and sealed in an anaerobic glove-box.

# 5.1 Measurements of the general corrosion rates

Assessing the long term general corrosion rate can be done using a variety of techniques, broadly characterized as active electrochemical techniques, or un-instrumented immersion experiments. Both approaches are described below.

#### Uninstrumented (weight-loss) method

Immersion testing is the simplest manner in which the general corrosion rate can be obtained. A variety of industry standard procedures exist defining this test, including the combination of ASTM G1 and ASTM G31. In essence, the sample is placed in the environment of concern for a fixed time period and observed upon completion of the test. To determine a corrosion rate from

such an experiment, the mass of the specimen is accurately measured prior to being placed into solution. At the completion of the test, the sample is descaled (removing all corrosion products while minimizing any removal of the base metal) and the weight of the specimen measured again. The weight change is then converted to a corrosion rate in terms of mass loss per unit area per time. This can be converted to a corrosion rate in terms of depth vs. time by using the density of the metal. The resolution of this measurement is the minimum measureable weight change per unit area of the sample per time. For passive metals, such as stainless steels, the general corrosion rate is very slow, defined by the passive current density. To measure the mass loss in these cases, longer reaction times are required. High precision balances, coupled with a well-defined measurement procedure, such as the NIST single substitution methods (NIST SOP no. 7), are needed.

#### Instrumented (electrochemical) method

Electrochemical testing can also be used to extract the general corrosion rate. This is accomplished by measuring the polarization resistance of the surface, then using the Stern-Geary equation. The procedure is described in ASTM G59, then the conversion of the polarization resistance to a corrosion rate in ASTM G102. The polarization resistance is determined by scanning the applied voltage across the open circuit potential. The magnitude of the applied potential must be sufficiently low that the voltage vs. current curve is linear (values of 5 to 20 mV are typical). The polarization resistance is then calculated as the slope of the voltage vs. current curve.

Polarization Resistance = 
$$R_P = \frac{\partial E}{\partial I} = \frac{\Delta E}{\Delta I}$$
 where  $\Delta E$  is small, and taken about  $E_{ocp}$ 

This polarization resistance is then converted to a corrosion current density, icorr, via the expression derived by Stern and Geary from the Nernst equation:

$$i_{corr} = \frac{B}{R_P}$$
 where  $B = \frac{b_a * b_c}{2.303 * (b_a + b_c)}$ 

Where B is the Stern-Geary constant, bathe anodic Tafel slope, and be the cathodic Tafel slope. A second set of experiments are required to acquire the Tafel slopes. Calculation of the Tafel slope requires that an anodic polarization experiment be performed on the material of interest to extract the anodic slope, and a cathodic polarization experiment for the cathodic slope. The applied potential is slowly scanned from near the open circuit potential in the desired direction. In most cases, a plot of the applied potential vs. the log of the current density will be linear, and the slope of this linear region is the Tafel slope:

$$b = \frac{\partial E}{\partial (\log(i))}$$

Once the anodic and cathodic Tafel slopes have been determined, the polarization resistance can be converted to the corrosion current density. For a pure metal, the oxidation reaction can be described as:

$$M \rightarrow M^{n+} + ne^-$$

In the case of an alloy, such as stainless steels, or Hastelloys, determination of the equivalent weight is more complicated as there are multiple constituents that will be part of the dissolution process. The nature of the individual reactions (in terms of the number of electrons passed for each constituent) will vary with the environment to which it is exposed. E-pH diagrams (i.e., Pourbaix diagrams (NACE 1974)) can be used to determine the likely valence states of each constituent, and values for common alloys are tabulated in ASTM G102.

Both electrochemical and immersion (weight loss) techniques can be effective at accurately measuring the general corrosion rate, but both have limitations, particularly when corrosion resistant materials such as stainless steels or nickel-chromium alloys are explored under conditions where their corrosion rates are very low (i.e., the materials are passive). We will use the aqueous chemistry data and chemical and mineralogical characterization of the corrosion products to guide the interpretation of the electrochemical data.

#### 5.2 Localized corrosion tests

Passive materials, such as stainless steels or nickel-chromium alloys, typically exhibit a very low general corrosion rate (defined by their passive current density). However, in the presence of aggressive ions such as chloride, thiosulfate, etc., they are prone to localized corrosion. Localized corrosion results from breakdown of the passive film, often at a microstructural heterogeneity such as a grain boundary or second phase precipitate, followed by focused dissolution of the underlying metal. This type of corrosion is generally manifested as pitting or crevice corrosion. Crevice corrosion is similar in many respects to pitting in terms of the reactions, externally located cathode, etc.; however, in the case of crevice corrosion, an occluded geometry (i.e., the crevice) provides the driving force for initiation. This mass transport limitation results in a gradual increase in the metal ion content and a decrease in the cathodic reactant within the crevice. Crevice corrosion is typically more readily initiated on susceptible materials than pitting.

#### *Un-instrumented exposures (not driven)*

As with general corrosion testing, immersion testing involves simply placing the samples into the desired environment for a predetermined time period, then removing and inspecting the sample for damage. In the case of pitting corrosion, samples are prepared and placed into solution such that no unintended crevices are formed. In the case of crevice corrosion, samples are instrumented such that an artificial crevice or crevices are formed on the metal surface. A general procedure for examination of localized corrosion is presented in ASTM G46.

#### Electrochemical approach (driven experiments)

Electrochemical methods for determining the potential for pitting or crevice corrosion involve the identification of a series of critical potentials, illustrated schematically in Figure 4. An anodic polarization curve is performed (the arrows in the figure indicate the direction with which the applied voltage is scanned), the general procedure for which is described in ASTM G5. As the potential becomes more positive, the driving force for oxidation to occur on the surface increases. At this point, the dissolution rate is low, and the slope of the polarization curve is large. The current density in this regime is the passive current density. Passive materials are often referred to as being highly polarizable due to this behavior – in other words, large shifts in the applied voltage result in vanishingly small changes in the oxidation rate at the metal surface.

When the applied potential becomes sufficiently large, local breakdown of the passive film results, and pitting initiates. On the polarization curve, this is manifested as a rapid increase in the measured current density as the applied voltage becomes increasingly positive. At that point, there are one or more stable pits propagating on the metal surface. The direction of the polarization scan is then reversed, and the scan begins moving to less positive potentials. Initially, the current density will remain large, as the pits remain stable. When the potential has reduced to a sufficiently low level, the current density will decrease to below the previously measured passive current density. The point at which the polarization curve crosses itself is referred to as the repassivation potential (indicating that the system is no longer actively propagating, and has returned to a state of passive dissolution.

Electrochemical crevice corrosion experiments are performed in essentially the same way. The sample is instrumented with a multiple crevice former or similar device, and potential at which a rapid increase in current is measured corresponds to the crevice corrosion initiation potential. The critical potential for crevice corrosion initiation is typically less positive than that of pitting.

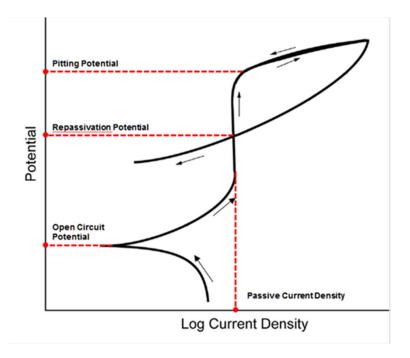


Figure 4. Schematic representation of an anodic polarization curve for a passive metal susceptible to localized corrosion. Indicated on the figure are the open circuit potential (i.e., the rest potential), the pitting potential, the repassivation potential, and the passive current density

# 5.3 Tests for the environmentally assisted cracking

In addition to corrosion at the metal surface, the components of the container or container internals may be susceptible to environmentally assisted cracking. There are two forms that are of concern in the considered failure/performance scenarios – stress corrosion cracking (SCC) and

hydrogen embrittlement. Stress corrosion cracking is, in many ways, analogous to localized corrosion in that there is an active corrosion front (i.e., the crack tip) and a cathodic area supporting that dissolution process, typically located at the metal surface (i.e., outside of the crack). In order for stress corrosion cracking to occur, the material must be susceptible to stress corrosion cracking, there must be a sufficiently aggressive environment, and, there must be a sufficiently large stress to support propagation of a crack. The goal of the proposed testing is to determine if the considered materials (stainless steels 304/304L and 316/316L, and Hastelloys C-4 and C-22) will crack under the stress load expected in a repository and upon exposure to the relevant groundwater compositions.

There are two aspects to the stress corrosion cracking process— the first is the nucleation behavior and the second is the propagation behavior. Nucleation is a particularly difficult aspect to study in a definitive manner, as there may be very long induction periods before cracking initiates. These induction periods can be associated with changes in the surface chemistry of the material or the initiation and propagation of other degradation modes, such as pitting, which result in a stress riser and serve as an initiation site. A variety of techniques have been employed to assess the risk of crack initiation, these include U-Bend specimens (ASTM G30), C-ring specimens (ASTM G38) and bent beam specimens (ASTM G39). Such specimens provide a pre-stressed specimen which can be exposed to a variety of aggressive environments.

In order to effectively measure crack growth rates, specimens which have a known stress state, and with awell-defined (and understood) crack geometry are needed. This is typically done using specimens and test techniques that mimic what is done when assessing the plane strain fracture toughness of materials. Procedures for this are generally defined in ASTM E399, E1304, and E1820. Crack growth rates are monitored via techniques such as direct current-potential drop (DCPD) where a large current is passed through the sample while being evaluated. The specimen acts as a resistor, with the voltage drop across the specimen increasing as the crack extends into the material. Experiments may be performed using traditional compact tension test specimens, as illustrated in ASTM E1820. Another method to perform SCC growth rate testing is through the use of double-cantilever beam specimens, as discussed in ASTM G168. The specimens are typically loaded through the use of bolts, and can be instrumented with DCPD or similar sensors to measure crack growth rate as a function of time, though often simple measurements of the crack length along the sample side are used to gauge the crack growth rate.

In many repository scenarios, cathodically generated hydrogen (accompanying metal oxidation) is anticipated to build in pressure, due to the low permeability of the surrounding overpack/buffer materials. As such, there is a concern that hydrogen embrittlement of the materials may occur. There are a variety of mechanisms through which hydrogen can adversely impact the mechanical properties of a metal. In general, the end result of hydrogen is a reduction in ductility and ultimate strength, and an overall more brittle nature of the cracking process. For austenitic stainless steels and nickel based alloys, the susceptibility to hydrogen embrittlement increases with increasing yield strength.

Title
12 Date

# 6. Summary and expected outcomes of the laboratory testing program

The investigated processes, which could potentially control the degradation rates of the stainless steel basket and the proposed overpack materials, are summarized below:

- General corrosion rates under anoxic conditions for stainless steels, and Hastelloys C-4 and C-22.
- Hydrogen embrittlement of the stainless steel canister under diffusion-controlled conditions if hydrogen gas is building up between the canister and the overpack do we expect embrittlement and enhanced corrosion?
  - Coupling between physical and chemical effects on the durability of stainless steel basket
- Critical pitting temperature of the Hastelloys C-4 and C-22 under geochemical conditions representative of the shale and granite repositories
- Chemical controls on the evolution of the passive film on the stainless steel and Hastelloys C-4 and C-22 under anaerobic conditions

The proposed experimental testing program is designed to illustrate whether structural integrity of a stainless steel basked will be preserved in case of an early breach (flooding with groundwater) of a DPC. Additionally, we are addressing several of the most uncertain areas concerning material behavior in a repository, particularly corrosion rates of the corrosion-resistant materials under anoxic conditions, potential for the localized corrosion and its feedback to the mechanical strength of the waste package components. The evaluated materials are stainless steels 304/304L and 316/316L – widely used in the existing DPCs, and prospective overpack materials Hastelloys C-4 and C-22. These results will contribute to the overall evaluations on the feasibility of the direct disposal of DPCs.

#### 7. References

ASTM E399 "Standard Test Method for Linear-Elastic Plane-Strain Fracture Toughness KIc of Metallic Materials"

ASTM E1304 "Standard Test Method for Plane-Strain (Chevron-Notch) Fracture Toughness of Metallic Materials"

ASTM E1820 "Standard Test Method for Measurement of Fracture Toughness"

ASTM F1459 "Standard Test Method for Determination of the Susceptibility of Metallic Materials to Hydrogen Gas Embrittlement (HGE)"

ASTM G1 "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens"

ASTM G5 "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"

ASTM G30 "Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens"

ASTM G31 "Standard Guide for Laboratory Immersion Corrosion Testing of Metals"

ASTM G38 "Standard Practice for Making and Using C-Ring Stress-Corrosion Test Specimens"

ASTM G39 "Standard Practice for Preparation and Use of Bent-Beam Stress-Corrosion Test Specimens"

ASTM G46 "Standard Guide for Examination and Evaluation of Pitting Corrosion"

ASTM G59 "Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements"

ASTM G102 "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements"

ASTM G168 "Standard Practice for Making and Using Precracked Double Beam Stress Corrosion Specimens"

Blondes, M.S., K.D. Gans, J.J. Thordsen, M.E. Reidy, B. Thomas, M.A. Engle, Y.K. Kharaka and E.L. Rowan 2014. U.S. Geological Survey National Produced Waters Geochemical Database v2.0 (Provisional), April, 2014.

Disposal criticality analysis methodology topical report (1998) YMP/TR-004Q. US DOE, Office of Civilian Radioactive Waste Management, Las Vegas, Nevada

Title
14 Date

Frape, S., A. Blyth, R. Blomqvist, R. McNutt and M. Gascoyne 2003. "5.17 Deep Fluids in the Continents: II. Crystalline Rocks." In: *Treatise on Geochemistry* (Eds. H. Holland, and K. Turekian). pp. 541-580.

Hardin E., Bryan C., Ilgen A., Kalinina E., Banerjee K., Clarity J., Howard R., Jubin R., Scaglione J., Perry F., Zheng L., Rutqvist J., Birkholzer J., Greenberg H., Carter J., Severynse T., FCRD-UFD-2014-000069 Rev. 0, August, 2014
Jové Colón C.F., Weck, P.F., Sassani D.H., Zheng L., Rutqvist J., Steefel C.I., Kim K., Nakagawa, S., Houseworth J., Birkholzer J., Caporuscio F.A., Cheshire M., Rearick M.S., McCarney M.K., Zavarin M., Benedicto A., Kersting A.B., Sutton M., Jerden J., Frey K.E., Copple J.M., and Ebert W. Evaluation of Used Fuel Disposition in Clay-Bearing Rock, FCRD-UFD-2014-000056, August, 2014

Kursten, B., E. Smailos, I. Azkarate, L. Werme, N.R. Smart and G. Santarini 2004. COBECOMA: State-of-the-art document on the COrrosion BEhaviour of COntainer MAterials. European Commission 5th Euratom Framework Programme, 1998-2002. Contract # FIKW-CT-20014-20138 Final Report: European Commission.

NACE, 1974: M. Pourbaix "Atlas of Electrochemical Equilibria in Aqueous Solutions", NACE International, 1974.

NIST SOP No. 7 "Recommended Standard Operating Procedure for Weighing by Single Substitution Using a Single-Pan Mechanical Balance, a Full Electronic Balance, or a Balance with Digital Indications and Built-In Weights".

NRC (US Nuclear Regulatory Commission). Spent fuel transportation risk assessment. NUREG-2125. Washington DC: Office of Nuclear Materials Safety and Safeguards, US Nuclear Regulatory Commission; 2014.